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**Vibrational Relaxation of HF( $v = 1$  and  $3$ ) in  $H_2$ ,  $N_2$ , and  $D_2$   
at 200 and 295 K**

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**1 February 1980**

**Interim Report**

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**Prepared for**  
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This interim report was submitted by The Aerospace Corporation, El Segundo, CA 90245, under Contract No. F04701-79-C-0080 with the Space Division, Deputy for Technology, P.O. Box 92960, Worldway Postal Center, Los Angeles, CA 90009. It was reviewed and approved for The Aerospace Corporation by W. R. Warren, Jr., Director, Aerophysics Laboratory. Lieutenant J. C. Garcia, SD/YLXT, was the project officer for Technology.


This report has been reviewed by the Public Affairs Office (PAS) and is releasable to the National Technical Information Service (NTIS). At NTIS, it will be available to the general public, including foreign nations.

This technical report has been reviewed and is approved for publication. Publication of this report does not constitute Air Force approval of the report's findings or conclusions. It is published only for the exchange and stimulation of ideas.

  
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SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

19 REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM	
1. REPORT NUMBER SD-TR-80-3	2. GOVT ACCESSION NO.	3. RECIPIENT'S CATALOG NUMBER	
4. TITLE (and Subtitle) VIBRATIONAL RELAXATION OF HF (v = 1 and 3) in H <sub>2</sub> , N <sub>2</sub> , and D <sub>2</sub> AT 200 AND 295 K.		5. TYPE OF REPORT & PERIOD COVERED Interim Repts	
6. AUTHOR(s) Jerry F. Bott Raymond F. Heidner		7. PERFORMING ORG. REPORT NUMBER TR-0080(5603)-27	
8. PERFORMING ORGANIZATION NAME AND ADDRESS The Aerospace Corporation El Segundo, Calif. 90245		9. CONTRACT OR GRANT NUMBER(s) F04701-79-C-0080	
10. CONTROLLING OFFICE NAME AND ADDRESS Air Force Weapons Laboratory Kirtland Air Force Base, N. Mex. 87117		11. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS 1226	
12. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office) Space Division Air Force Systems Command Los Angeles Air Force Station Los Angeles, Calif. 90009		13. REPORT DATE 1 Feb 80	
14. DISTRIBUTION STATEMENT (of this Report) Approved for public release; distribution unlimited.		15. NUMBER OF PAGES 25	
16. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)		17. SECURITY CLASS. (of this report) Unclassified	
18. SUPPLEMENTARY NOTES		19a. DECLASSIFICATION/DOWNGRADING SCHEDULE	
19. KEY WORDS (Continue on reverse side if necessary and identify by block number) Chemical Kinetics Chemical Laser Hydrogen Fluoride Vibrational Deactivation			
20. ABSTRACT (Continue on reverse side if necessary and identify by block number) The vibrational relaxation rates of HF (v = 1) and HF (v = 3) have been measured in H <sub>2</sub> , N <sub>2</sub> , and D <sub>2</sub> at 200 and 295 K. The v dependence of the relaxation rates is essentially the same for N <sub>2</sub> , D <sub>2</sub> , and several other diatomic molecules that deactivate HF by exothermic processes. The rates for HF (v = 3) deactivation are larger than those for HF (v = 1) by a factor of ~18 at both 200 and 295 K. Labaut			

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## I. INTRODUCTION

In recent studies,<sup>1-4</sup> the rate coefficients for the deactivation of the upper vibrational levels of HF and DF were found to scale more strongly with  $v$  than the  $k_v \propto v$  scaling predicted for harmonic oscillators. The present studies have been performed at reduced temperatures to determine if the  $v$  dependence of the HF rate coefficients is sensitive to temperature in the range of 200 to 295 K.

The pumping reaction



directly populates  $v = 1, 2$ , and  $3$ , so that the scaling of the  $\text{HF}(v)$  deactivation rates with  $v$  is important for understanding the detailed performance of the HF chemical laser. In previous studies,<sup>2,3</sup> the rate coefficients at 295 K were found to scale as  $v^n$  with  $n = 2.7 \pm 0.2$  for  $\text{HF}(v = 1, 2, 3)$  in  $\text{N}_2$ ,  $\text{O}_2$ , and  $\text{HCl}$ , and  $n = 1.9 \pm 0.1$  for  $\text{DF}(v = 1-4)$  in  $\text{H}_2$ ,  $\text{HF}$ , and  $\text{N}_2$ . For comparison, we have measured deactivation rates of  $\text{HF}(v = 1 \text{ and } 3)$  in  $\text{H}_2$ ,  $\text{D}_2$ , and  $\text{N}_2$  at 200 K.

## II. EXPERIMENT

The experiments were performed in the fluorescence cell that was used for a study of H-atom deactivation of  $\text{HF}(v = 3)$  and  $\text{HF}(v = 2)$ .<sup>5,6</sup> The reports of those studies contain the details of the time-resolved infrared signal processing, the TEA HF pulsed laser, and the cooled fluorescence cell. An RCA C-31034 (GaAs) photomultiplier and an InSb detector were used to monitor the fluorescence of  $\text{HF}(v = 3)$  at  $0.89 \mu\text{m}$  and that of  $\text{HF}(v = 1)$  at  $2.5$  to  $3.0 \mu\text{m}$ , respectively. Narrow band filters restricted the fluorescence to a  $0.02\text{-}\mu\text{m}$  spectral band centered at  $0.89 \mu\text{m}$  for  $v = 3$  and to a  $0.5\text{-}\mu\text{m}$  spectral band centered at  $2.75 \mu\text{m}$  for  $v = 1$ .

The gases included hydrogen (Matheson 99.95%), nitrogen (Air Products 99.998%), deuterium (Precision Gas Products 98%), helium (Air Products 99.995%), and HF (Matheson 99.9%). The HF was purified by pumping at 77 K to remove the noncondensibles before distillation into a passivated stainless steel cylinder. The HF, diluted 1:10 with helium, was metered into the flow tube-fluorescence cell with a calibrated needle valve. The needle valve and Matheson rotating ball flowmeters used to meter the other gases were calibrated by pressure-rise measurements in a standard volume.

Experiments were performed at various flow rates of the collision partners with the HF-helium flow adjusted to give HF partial pressures of  $\sim 1.5 \times 10^{-3}$  Torr. At this partial pressure, the self-deactivation rate of  $\text{HF}(v = 1)$  is  $1 \times 10^{-4} \mu\text{sec}^{-1}$  at 295 K and  $2 \times 10^{-4} \mu\text{sec}^{-1}$  at 200 K.<sup>7</sup> These rates are small contributions to the measured decay rates of  $\text{HF}(v = 1)$ . The deactivation rate of  $\text{HF}(v = 3)$  by HF is  $\sim 20$  times larger<sup>1,4</sup> than that of  $\text{HF}(v = 1)$  ( $\sim 2 \times 10^{-3} \mu\text{sec}^{-1}$  at 295 K and  $\sim 4 \times 10^{-3} \mu\text{sec}^{-1}$  at 200 K). The measurements of  $\text{HF}(v = 3)$  deactivation rates were obtained for a wide range of quenching pressures in order to minimize the contributions of self-deactivation and diffusion.

### III. RESULTS

Single exponential decay rates were determined from the fluorescence traces. These data for HF( $v = 1$ ) and HF( $v = 3$ ) are plotted versus the pressures of H<sub>2</sub>, N<sub>2</sub>, and D<sub>2</sub> in Figs. 1 through 6. The deactivation rate coefficients determined from the slopes of the lines through the data are listed in Table 1. For a discussion of the equations governing the deactivation of the several vibrational levels following laser excitation, see Ref. 2.

#### A. DEACTIVATION by H<sub>2</sub>

The deactivation rates for HF( $v = 3$ ) in H<sub>2</sub> have a small but measurable contribution from diffusion at 1 Torr. When 10 Torr of helium was added to a hydrogen partial pressure of 1.05 Torr, the deactivation rate decreased from 0.023 to 0.016  $\mu\text{sec}^{-1}$ , a value in agreement with an extrapolation of the higher pressure data of Fig. 2.

The present value of  $(1.69 \pm 0.17) \times 10^{-2}$  for the rate coefficient for HF( $v = 1$ ) deactivation by H<sub>2</sub> at 295 K compares favorably with values of  $(1.43 \pm 0.15) \times 10^{-2}$  and  $(1.7 \pm 0.1) \times 10^{-2} (\mu\text{sec Torr})^{-1}$  obtained previously in this laboratory.<sup>2,8</sup> Several other literature values are listed in Ref. 8. The present value of  $(1.13 \pm 0.12) \times 10^{-2} (\mu\text{sec Torr})^{-1}$  for the HF( $v = 3$ )-H<sub>2</sub> deactivation rate coefficient at  $T = 295$  K is identical to that reported in Ref. 2 and is larger than the value of  $(0.90 \pm 0.10) \times 10^{-2} (\mu\text{sec Torr})^{-1}$  obtained at 200 K. For the purpose of comparing rates measured at different temperatures, the probability of collisional deactivation has been calculated using collision diameters of 2.55 Å for HF and 2.9 Å for H<sub>2</sub>. In Fig. 7, these probabilities,  $P$ , are plotted versus  $1/T$  for comparison with data obtained from laser-induced fluorescence experiments performed behind reflected shock waves at 295 to 1000 K.<sup>8</sup> The data for HF( $v = 1$ ) may be fitted by the expression  $P = 1.57 \times 10^{-3} \exp(-84/T)$ . It should be noted that this process is endothermic by 201  $\text{cm}^{-1}$  (289 K) so that the probability of the reverse, exothermic process is given by  $P = 1.57 \times 10^{-3} \exp(205/T)$ .



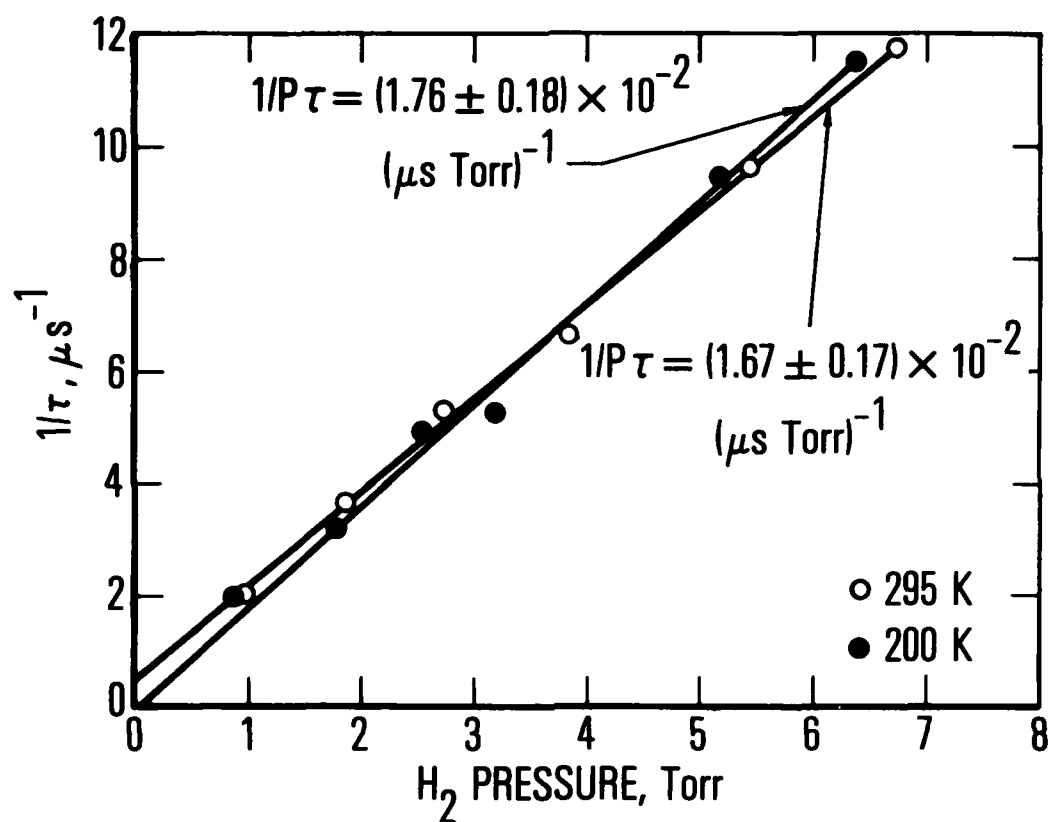


Figure 1. Relaxation Rates of  $HF(v = 1)$  versus  $H_2$  Pressure at 200 and 295 K

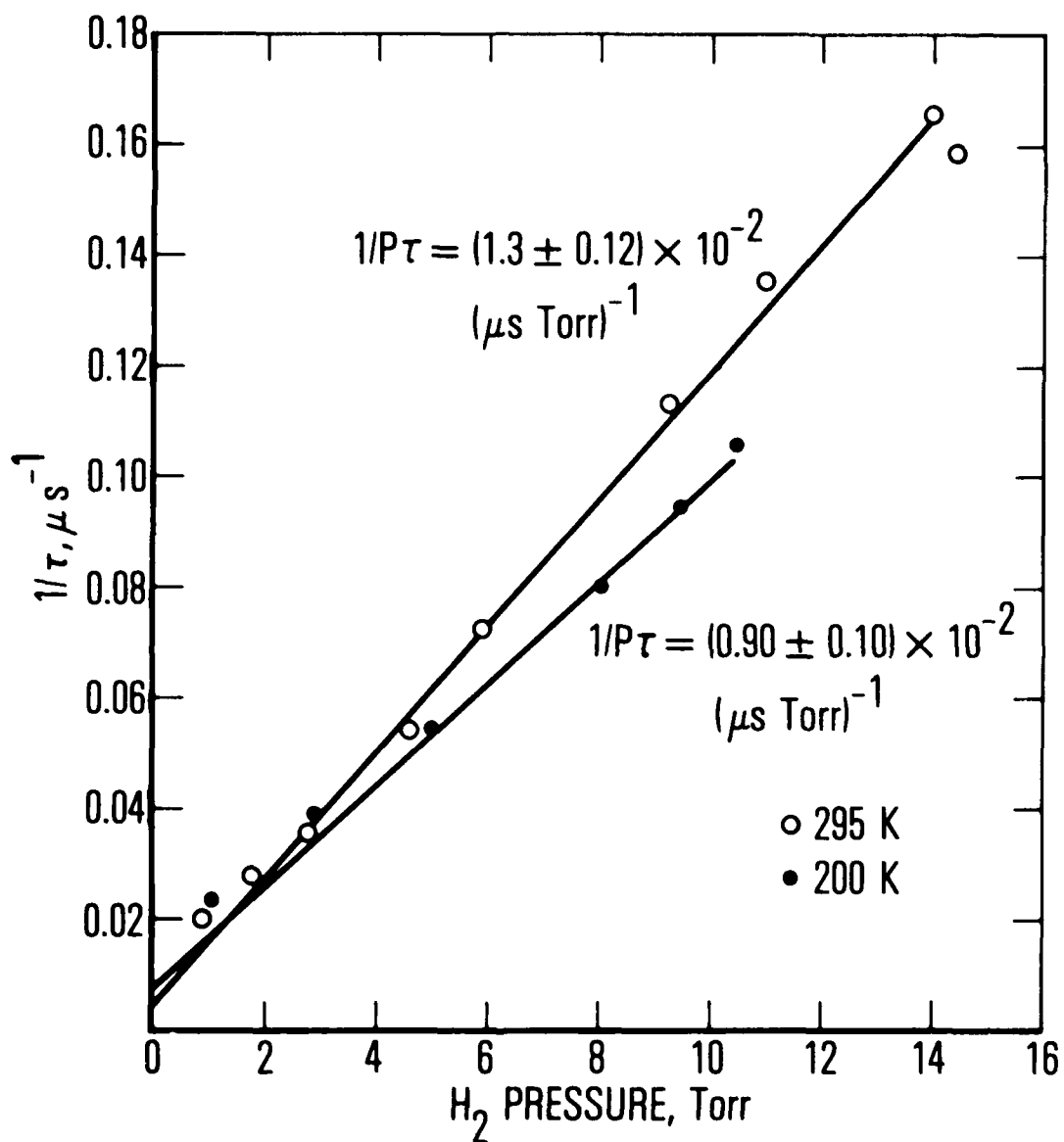


Figure 2. Relaxation Rates of HF( $v = 3$ ) versus  $H_2$  Pressure at 200 and 295 K

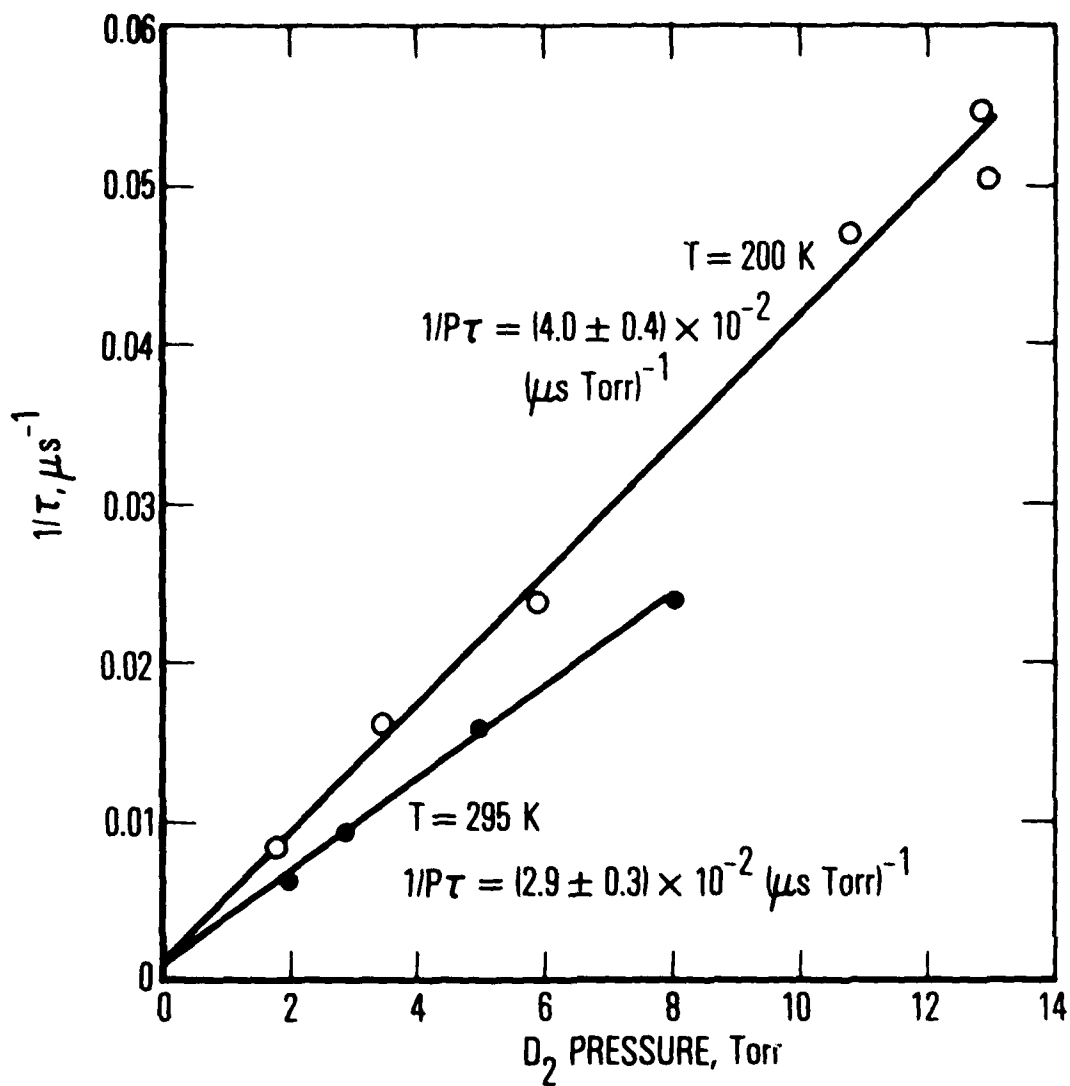


Figure 3. Relaxation Rates of  $HF(v = 1)$  versus  $D_2$  Pressure at 200 and 295 K

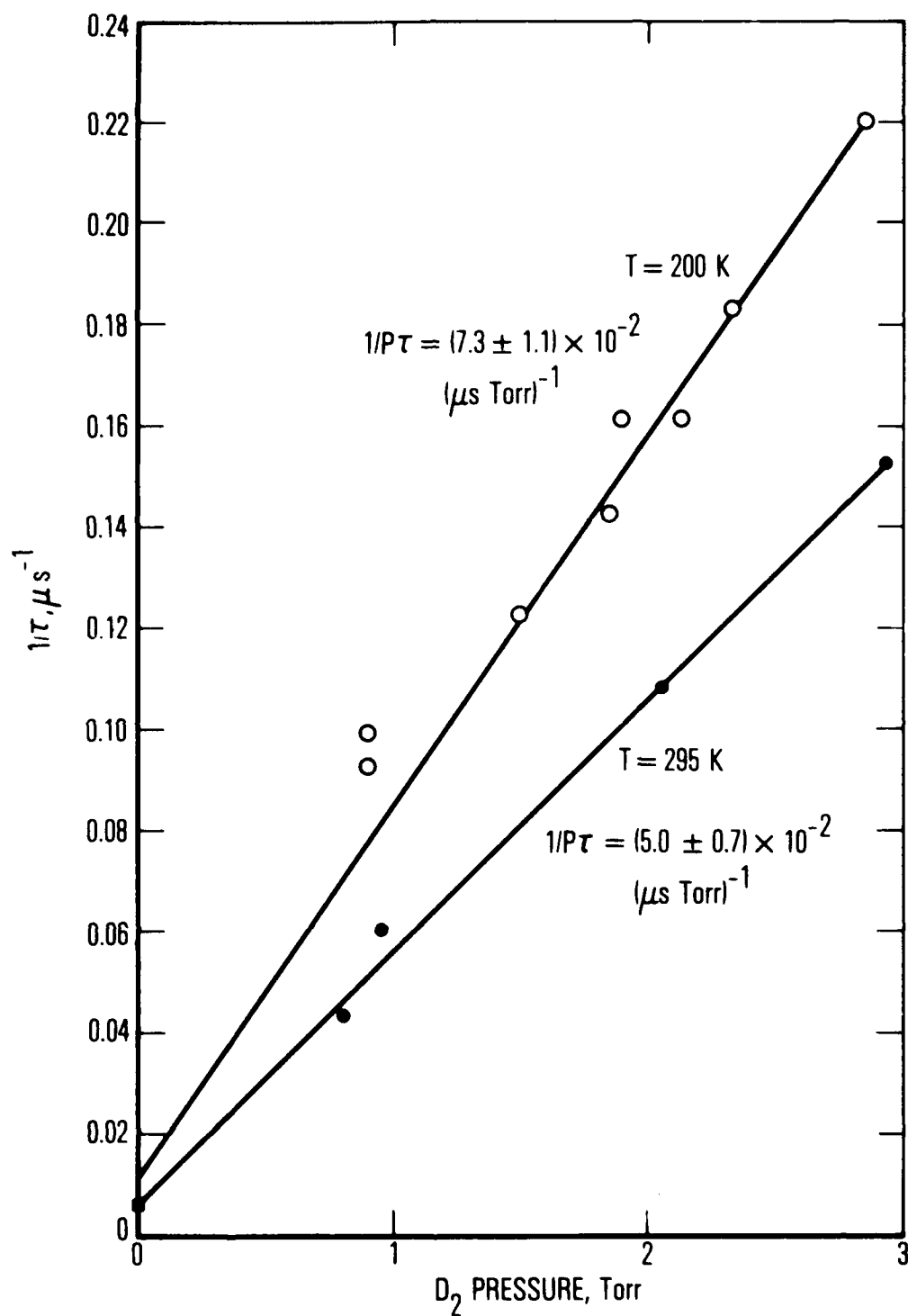


Figure 4. Relaxation Rates of HF( $v = 3$ ) versus  $D_2$  Pressure at 200 and 295 K

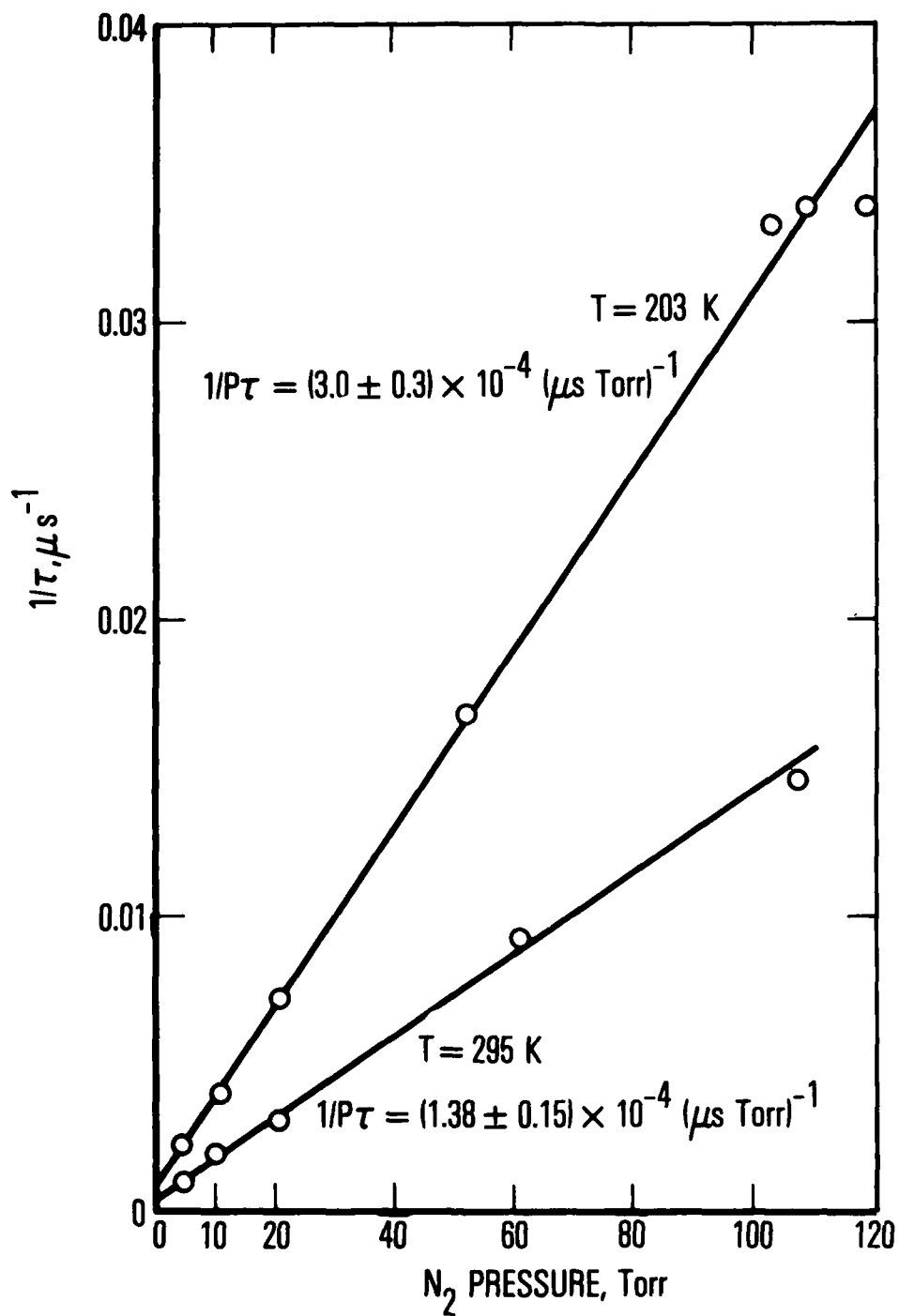


Figure 5. Relaxation Rates of  $HF(v = 1)$  versus  $N_2$  Pressure at 203 and 295 K

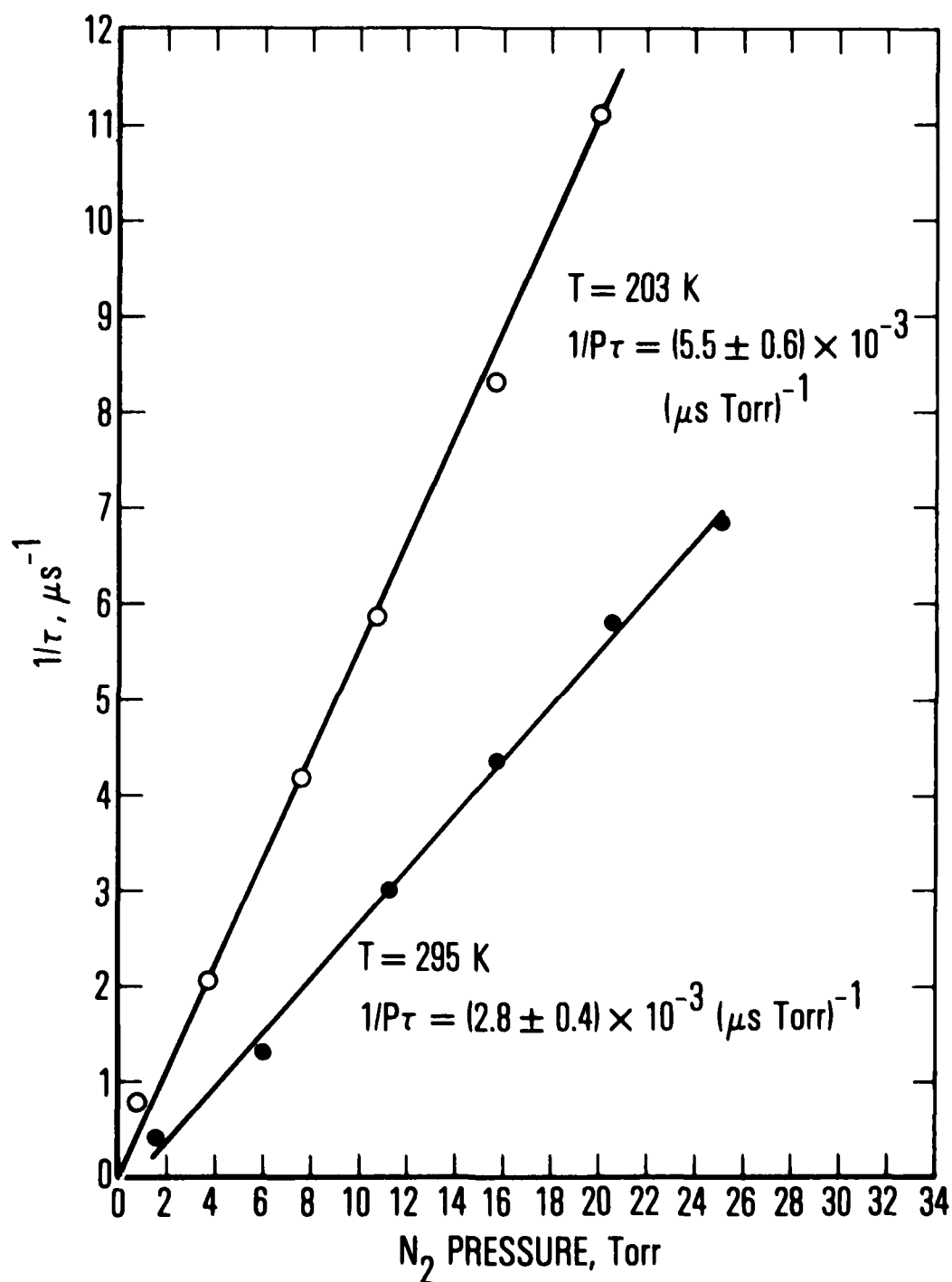


Figure 6. Relaxation Rates of  $\text{HF}(v = 3)$  versus  $\text{N}_2$  Pressure at 203 and 295 K

Table 1. Deactivation Rate Coefficients, ( $\mu\text{sec-Torr}$ )<sup>-1</sup>

	295 K	200 K
HF(v = 1)-H <sub>2</sub>	$(1.67 \pm 0.17) \times 10^{-2}$	$(1.76 \pm 0.18) \times 10^{-2}$
HF(v = 3)-H <sub>2</sub>	$(1.13 \pm 0.12) \times 10^{-2}$	$(0.90 \pm 0.10) \times 10^{-2}$
HF(v = 1)-N <sub>2</sub>	$(1.38 \pm 0.15) \times 10^{-4}$	$(3.0 \pm 0.3) \times 10^{-4}^a$
HF(v = 3)-N <sub>2</sub>	$(2.85 \pm 0.4) \times 10^{-3}$	$(5.5 \pm 0.6) \times 10^{-3}^a$
HF(v = 1)-D <sub>2</sub>	$(2.9 \pm 0.3) \times 10^{-3}$	$(4.0 \pm 0.4) \times 10^{-3}$
HF(v = 3)-D <sub>2</sub>	$(5.0 \pm 0.7) \times 10^{-2}$	$(7.3 \pm 1.1) \times 10^{-2}$

<sup>a</sup>T = 203  $\pm$  4 K.

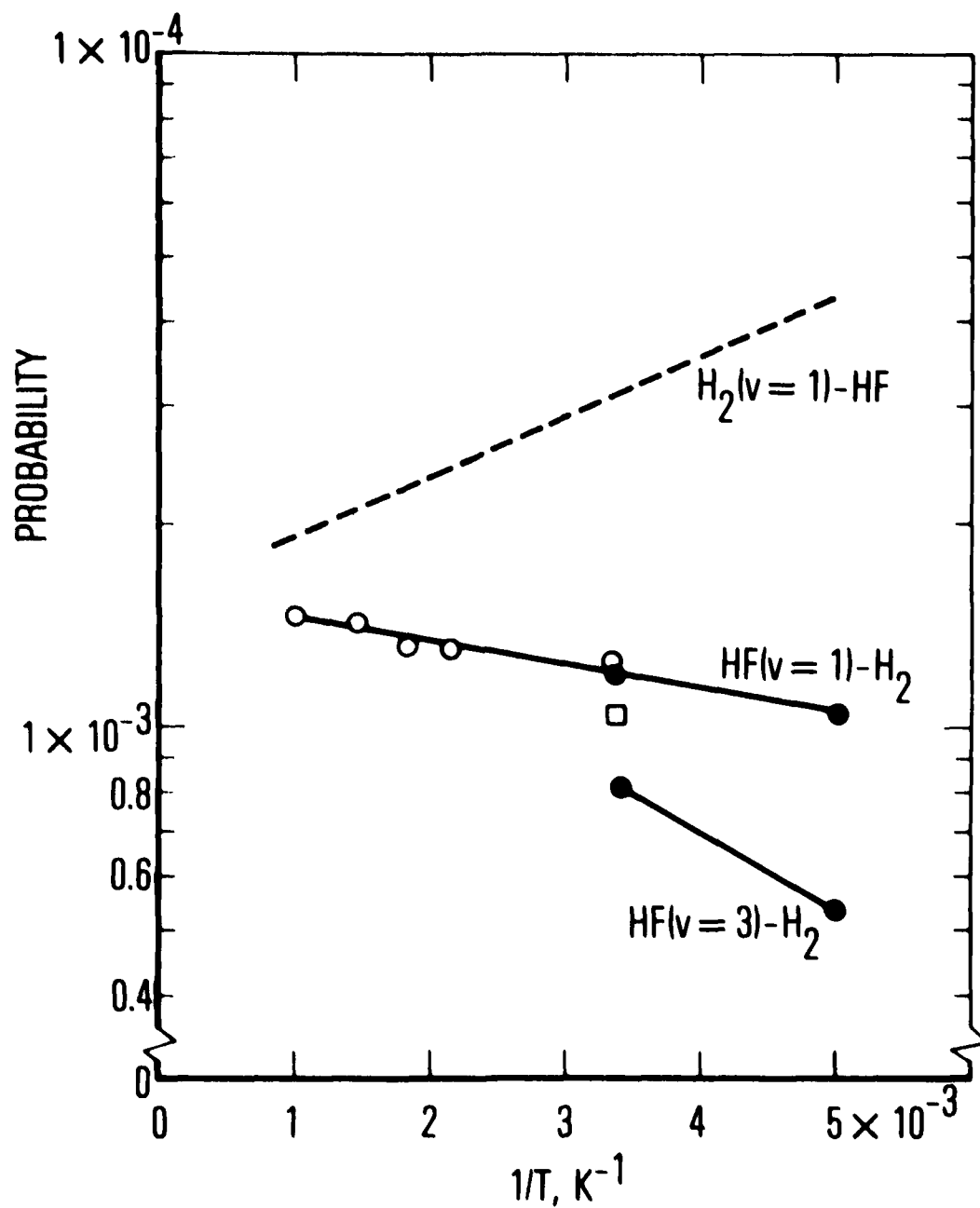


Figure 7. Deactivation Probabilities for HF( $v = 1$ ) and HF( $v = 3$ ) in H<sub>2</sub> versus Reciprocal Temperature.  $\circ$ ;  $\square$ ;  $\bullet$ , present data; —, exothermic exchange probability for H<sub>2</sub> ( $v = 1$ )-HF, see discussion



### B. DEACTIVATION by D<sub>2</sub>

The fit to the HF( $v = 3$ )-D<sub>2</sub> data at  $T = 295$  K (Fig. 4) shows no discernible effect of diffusion at the lowest pressure ( $\sim 1$  Torr) studied. The present value of  $(2.9 \pm 0.3) \times 10^{-3} (\mu\text{sec Torr})^{-1}$  for the rate coefficient for HF( $v = 1$ ) deactivation by D<sub>2</sub> at 295 K compares with previously measured values of  $(3.1 \pm 0.6) \times 10^{-3}$  (Ref. 8) and  $(3.7 \pm 0.4) \times 10^{-3}$  (Ref. 9). The value of  $(5.0 \pm 0.7) \times 10^{-2} (\mu\text{sec Torr})^{-1}$  for the rate coefficient for HF( $v = 3$ ) deactivation by D<sub>2</sub> is in good agreement with the value of  $(4.4 \pm 0.8) \times 10^{-2}$  reported by Douglas and Moore.<sup>10</sup> The probabilities of HF( $v = 1$ ) deactivation by D<sub>2</sub> plotted versus  $1/T$  in Fig. 8 were calculated using a collision diameter of 2.9 Å for D<sub>2</sub>. These probabilities show a complex temperature dependence with a minimum near 300 K. The probability of deactivation,  $P$ , can be described with  $P = 1.74 \times 10^{-4} (T/295)^{1/2} \exp(152/T)$  for temperatures between 200 and 1000 K.

### C. DEACTIVATION by N<sub>2</sub>

The present value of  $(1.38 \pm 0.15) \times 10^{-4} (\mu\text{sec Torr})^{-1}$  for the rate coefficient for HF( $v = 1$ ) deactivation by N<sub>2</sub> at 295 K compares with previously measured values of  $(1.25 \pm 0.6) \times 10^{-4}$  (Ref. 9),  $(1.52 \pm 0.15) \times 10^{-4}$  (Ref. 8), and  $(1.45 \pm 0.15) \times 10^{-4}$  (Ref. 2). The present value of  $(2.85 \pm 0.40) \times 10^{-3} (\mu\text{sec Torr})^{-1}$  for the HF( $v = 3$ ) deactivation rate coefficient at 295 K is in good agreement with the previously reported<sup>2</sup> value of  $(2.92 \pm 0.30) \times 10^{-3}$ .

Probabilities for HF( $v = 1$ ) removal by N<sub>2</sub> were calculated from the data using a collision diameter of 3.7 Å for N<sub>2</sub>; these values are plotted versus  $1/T$  in Fig. 9. The trend displayed in the data for HF( $v = 1$ ) removal by D<sub>2</sub> is accentuated in Fig. 9 with the probability having a more pronounced minimum and rising more steeply with temperature above 1000 K. Empirically, these data may be described by the equation  $P = (9.4 \times 10^{-2} T^{-3/2} + 18 \times 10^{-13} T^{2.5})$  for  $T = 200$  to 1600 K. The removal probability passes through a minimum near 420 K. More importantly, this behavior, which is a common feature of hydrogen halide quenching,<sup>8</sup> suggests that more than one mechanism is responsible for HF( $v = 1, 3$ ) deactivation by the molecules H<sub>2</sub>, D<sub>2</sub>, and N<sub>2</sub>.

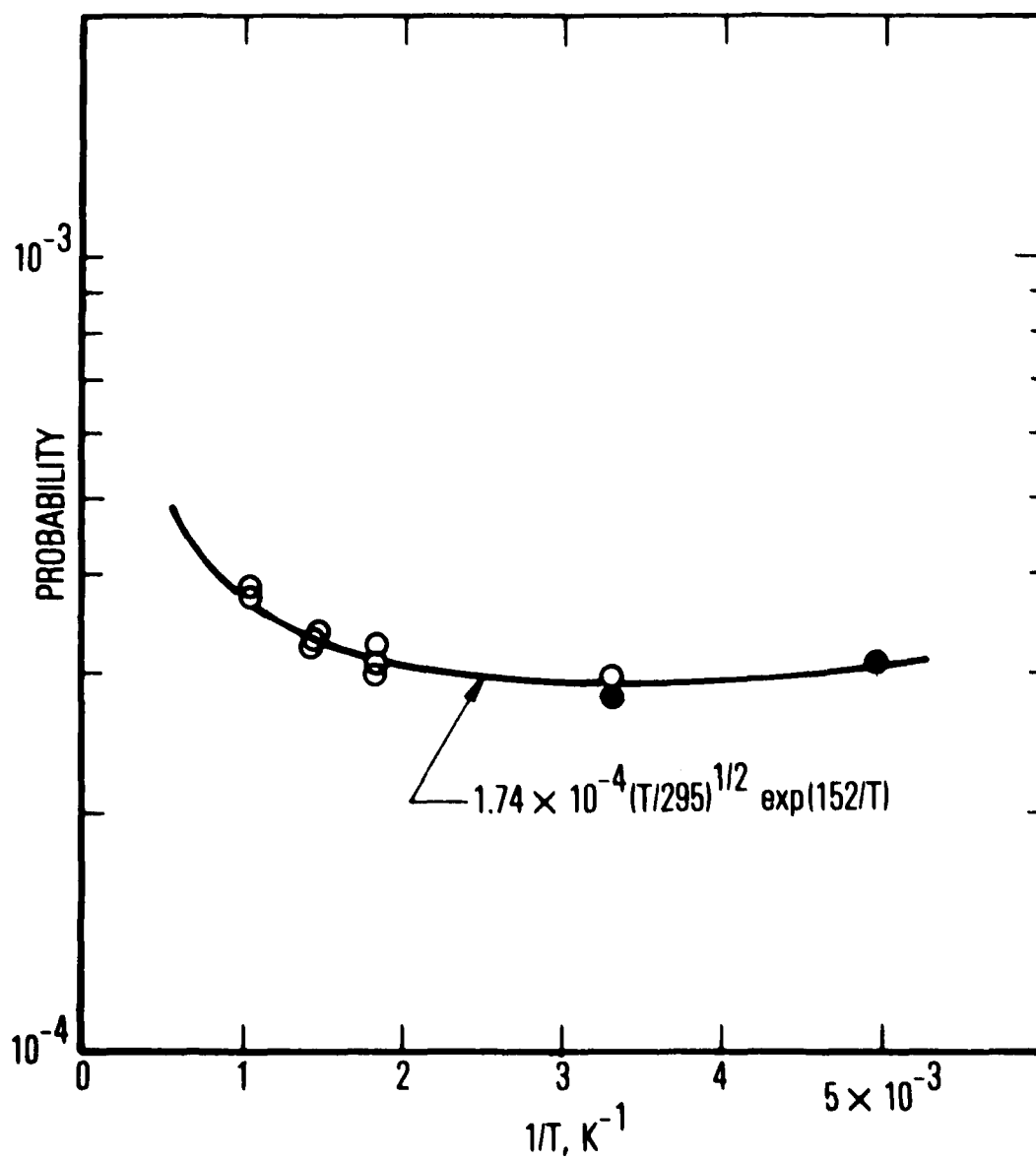


Figure 8. Deactivation Probabilities for HF( $v = 1$ ) in D<sub>2</sub> versus Reciprocal Temperature. ○ - Ref. 8, ● - present data

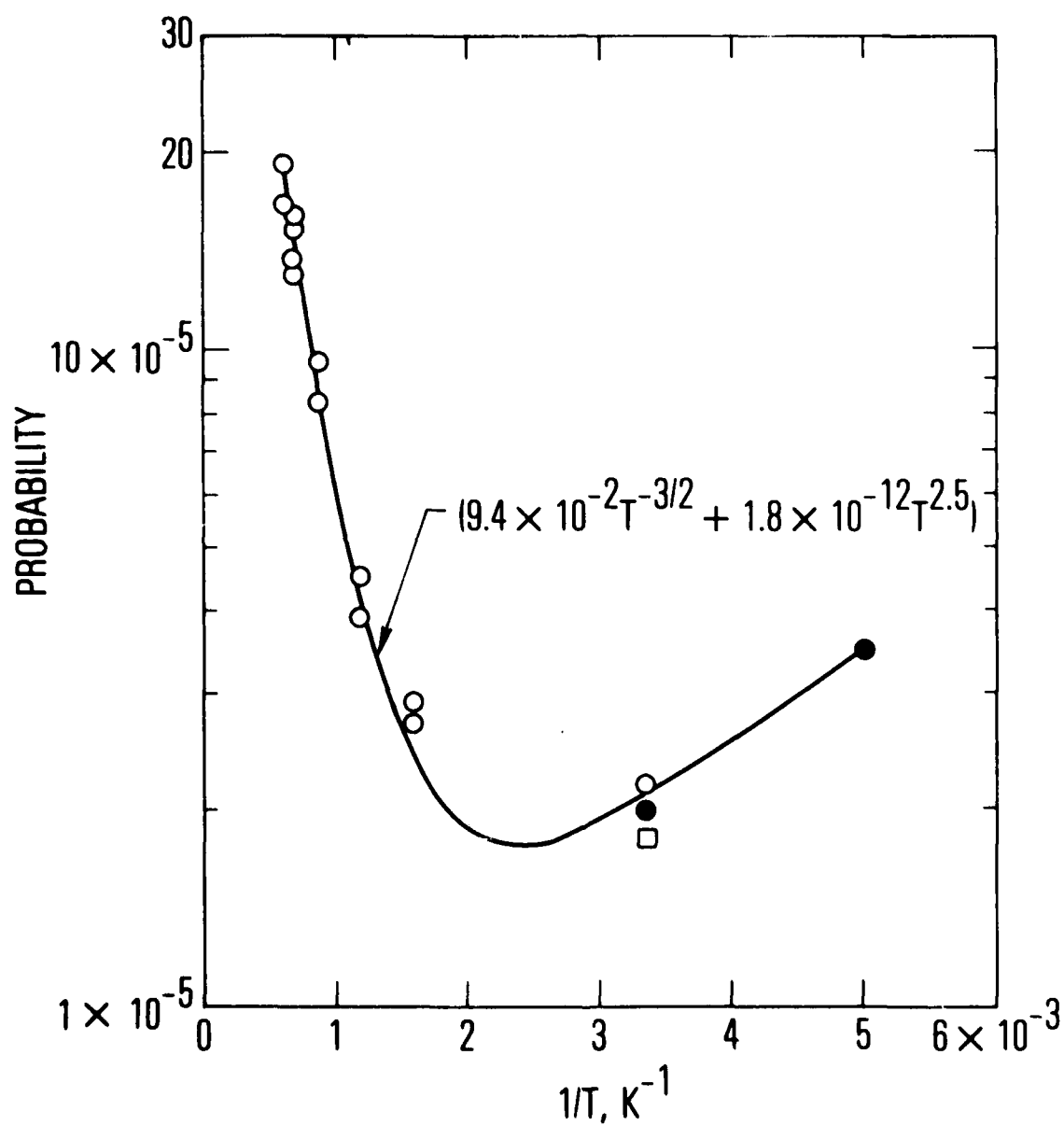


Figure 9. Deactivation Probabilities for HF( $v = 1$ ) in N<sub>2</sub> versus Reciprocal Temperature. ○ :<sup>8</sup> □ :<sup>9</sup> ● , present data

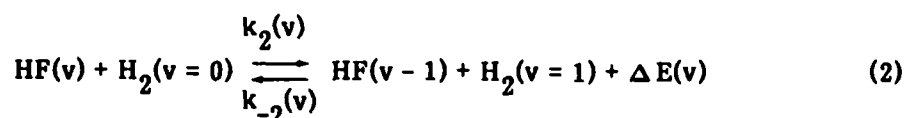
#### IV. DISCUSSION

A large body of high-temperature work<sup>11,12</sup> suggests that HF( $v = 1$ ) is relaxed with a rate coefficient that increases with increasing temperature. Several models have been used to describe these data, including the Landau-Teller formulation, which predicts that  $(P\tau)^{-1}$  is proportional to  $\exp(-AT^{-1/3})$ . Although some success has been realized with this approach at temperatures above 1300 K, the relaxation data studied to date exhibit a more complex behavior at lower temperatures. The rates for HF( $v = 1$ ) deactivation by  $H_2$ ,  $D_2$ ,  $DF$ ,  $HCl$ , and  $N_2$  (and for HF self-relaxation) show an inverse temperature dependence in certain temperature ranges.<sup>8</sup> The probability of HF self-relaxation has a negative temperature dependence below about 1200 K, and  $HCl$  and  $HBr$  self-relaxation probabilities show a similar behavior below about 400 K.<sup>13</sup> The temperatures at which these probability minima occur are approximately proportional to the binding energies for the respective dimers, and the large attractive interactions of the hydrogen halides have been used to explain qualitatively the low temperature inverse temperature dependence.

The attractive interactions can lead to long-lived bimolecular collisions or to the formation of excited complexes. Zittel and Moore<sup>11</sup> discussed the effect of attractive interactions on collisions with large impact parameters, where the rate of collisions surmounting any centrifugal barrier and experiencing a repulsive collision increases with decreasing temperature, relative to the rate of hard sphere collisions. Shin<sup>14,15</sup> used a collision model to calculate HF and DF self-relaxation rates and attributed the low-temperature behavior of the relaxation rates to collisions in which a loosely bound nonrigid dimer is formed at low temperatures. The vibrational energy of the initially excited molecule is transferred partly to hindered rotational motion and partly to back and forth translational motion. Long-lived complexes have been observed in classical trajectory studies over surfaces with sufficient well depths. Billing and Poulsen<sup>16</sup> found trajectories in which the molecules stick together and collide more than once. These "orbiting" collisions contributed significantly to the deactivation of HF( $v = 1$ ) at low tempera-

tures and resulted in large changes of angular momentum. On the other hand, in the classical trajectory study by Wilkins,<sup>17</sup> the vibrational energy was converted to rotational energy of the initially excited HF molecule by means of a V→R energy transfer process without orbiting collisions.

The deactivation of HF(v) by N<sub>2</sub>, H<sub>2</sub>, and D<sub>2</sub> can result in the vibrational excitation of the collision partner with the residual energy going into rotation of HF as well as relative translation. The potentials of interaction between polar HF and N<sub>2</sub>, H<sub>2</sub>, and D<sub>2</sub> are much smaller than between HF and HF, and the probabilities of HF(v = 1) deactivation by N<sub>2</sub>, D<sub>2</sub>, DF, and HCl have minima at lower temperatures than HF self-relaxation. For HF(v)-H<sub>2</sub> collisions, V→V exchange can occur by



Process (2) is endothermic by only 201 cm<sup>-1</sup> for v = 1 so that the vibrational energy exchange requires only a small conversion of rotational-translational energy. On the other hand, the V-R,T deactivation of HF(v = 1) by H<sub>2</sub> requires the conversion of ~3960 cm<sup>-1</sup> to rotational energy and has a rate coefficient of ≤ 3.8 × 10<sup>-4</sup> (μsec Torr)<sup>-1</sup> at 295 K.<sup>18</sup> Both the probability for Process (2) and the probability for the reverse, exothermic Process (-2) have been plotted in Fig. 7, neglecting the small V-R,T contribution. The exothermic probability is described by P = 1.57 × 10<sup>-3</sup> exp(205/T) between 200 and 1000 K. Any minimum in the H<sub>2</sub>-HF exchange probability must occur at a temperature greater than 1000 K.

If the entire deactivation rate for HF(v = 3) by H<sub>2</sub> is assigned to Process (2), then the reverse exothermic exchange also has an inverse temperature dependence. However, Poole and Smith<sup>1</sup> explained the v dependence of the total deactivation rate coefficient with a V-R,T contribution that increases with v and a V-V exchange contribution that decreases with v. If the rate coefficients for V-R,T deactivation of HF(v) by H<sub>2</sub> have the same v dependence as those found for other diatomic molecules, the V-R,T contribution to the deactivation of HF(v = 3) by H<sub>2</sub> at 295 K could be as much as 19 × 3.8 × 10<sup>-4</sup> = 7.2 × 10<sup>-3</sup> (μsec Torr)<sup>-1</sup> or 64% of the total rate coefficient.

When vibrational energy is transferred from  $\text{HF}(v = 1)$  to  $\text{D}_2(v = 1)$  or  $\text{N}_2(v = 1)$ , the excess energy of  $968 \text{ cm}^{-1}$  or  $1627 \text{ cm}^{-1}$ , respectively, must be accommodated by rotational and translational degrees of freedom. The  $\text{HF}(v = 1)$  deactivation probabilities decrease with increasing energy mismatch ( $\text{H}_2$ ,  $\text{D}_2$ ,  $\text{N}_2$ ,  $\text{O}_2$ ). The probability of  $\text{HF}(v = 1)$  deactivation by  $\text{D}_2$  is almost constant between 200 and 1000 K with a shallow minimum near 300 K (Fig. 8). The probability of  $\text{HF}(v = 1)$  deactivation by  $\text{N}_2$  has a much more pronounced minimum near 420 K (Fig. 9). Sentman and Solomon<sup>19</sup> have compared theoretical V-V exchange rates at room temperature and above. The theoretical calculations gave good agreement with experimental data above  $\sim 700 \text{ K}$  but did not contain long-range interactions that are the dominant contribution to the deactivation rates at low temperatures.

The rates for the deactivation of  $\text{HF}(v = 1,3)$  by  $\text{D}_2$  and  $\text{N}_2$  scale with  $v$  as  $v^{2.7 \pm 0.1}$  at both 295 and 200 K (see Table 2). The rate for  $\text{HF}(v = 4)$  deactivation in  $\text{D}_2$  obtained by Douglas and Moore<sup>10</sup> at 293 K is also consistent with this scaling. Although the nature of the collision partner does not affect this  $v$  dependence, it does affect the magnitude of the quenching probabilities. The same conclusion was reached in a study of  $\text{DF}(v)$  deactivation<sup>3</sup> although a  $v^{1.9 \pm 0.1}$  dependence holds in the case of  $\text{DF}$ . The exceptions are the endothermic V-V exchanges  $\text{HF}(v) \rightarrow \text{H}_2$  and  $\text{DF}(v) \rightarrow \text{D}_2$ . The same  $v$  dependence may not hold at higher temperatures where short-range interactions become more important and distributions over rotational levels shift toward higher states.

Table 2. Ratios of the Deactivation Rates  $k(v = 3)/k(v = 1)$

	295 K	200 K
H <sub>2</sub>	0.68, 0.79 <sup>a</sup>	0.51
N <sub>2</sub>	20.7, 20 <sup>a</sup>	18
D <sub>2</sub>	17.2	18
O <sub>2</sub>	≥ 16.7	
HCl	23.5 <sup>b</sup>	
HF	17 <sup>c</sup>	

<sup>a</sup>Ref. 2.

<sup>b</sup>HF(v = 3)-HCl data of Ref. 2,  $1.7 \times 10^{-2} (\mu \text{ sec Torr})^{-1}$  for HF(v = 1)-HCl.

<sup>c</sup>HF(v = 3)-HF data of Ref. 4,  $5.8 \times 10^{-2} (\mu \text{ sec Torr})^{-1}$  for HF(v = 1)-HF.

## V. CONCLUSIONS

The temperature dependence of  $\text{HF}(v = 1)$  deactivation by  $\text{N}_2$  and  $\text{D}_2$  below room temperature differs markedly from that at high temperatures. At low temperatures, the deactivation probabilities are rather small with a zero or small inverse temperature dependence in contrast to the positive dependence at higher temperatures.  $\text{HF}(v = 3)$  is quenched  $\sim 18$  times more rapidly than  $\text{HF}(v = 1)$  by both  $\text{N}_2$  and  $\text{D}_2$  at 200 and 295 K and by  $\text{HCl}$  and  $\text{O}_2$  at 295 K. For the near-resonant exothermic exchange between  $\text{H}_2(v = 1)$  and  $\text{HF}(v = 0)$ , Process (-2), the deactivation probabilities are much larger and show a small inverse temperature dependence. The detailed interpretation of the  $v$  dependence of  $\text{HF}(v)$  quenching by  $\text{H}_2$  is obscured by the increasing endothermicity with  $v$  and possible contributions of V-R,T deactivation of the higher vibrational levels. Further experiments are required to establish the vibrational scaling of  $\text{HF}(v)$  deactivation at higher temperatures.



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